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The effect of infrared pulsated laser on the degree of ordering of cellulose nitrate

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Abstract : The effect of infrared laser pulses on the degree of ordering of cellulose nitrate (LR-115) detector has been investigated X-ray diffraction measurements were carried out on LR-115 solid samples These samples were exposed to laser pulses with different exposure doses ranging from 0.0 to 7 5 J/cm^2. The dependence of the integral intensity of the amorphous regions (I_{am}), the integral intensity of the crystalline regions (I_{cr}), index of crystallinity (ω_c) and the crystallite size (L) on the laser dose was also studied. The absorbance of the LR-115 samples in the infrared range was also investigated The results indicated that a higher degree of ordering could be obtained when irradiating the LR-115 samples by infrared laser pulses up to 7.5 J/cm^2.

Keywords : Infrared pulsated laser, cellulose nitrate, X-ray diffraction and infrared spectra.

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1. Introduction

The problem of laser damage attains progressively more and more interest from researches due to the ever increasing important applications of laser technology. Fleske *et al* [1] focused a laser beam on the polymer surface, giving pulses once a second. This allowed exposure spectra to superimpose and permitted a survey of the material surface uniformly. Ready [2] studied the damage threshold in different transparent solid materials. There was a difference between the damage threshold at the surface and the damage threshold when the point was in the interior of the sample. Patel and Baisch [3] studied the effect of incident laser fluence, laser frequency, and polymer thickness on a single pass cutting speed. Keiko *et al* [4] studied the photoablating behaviour of various polymers irradiated by excimer lasers and YAG lasers. Experiments reveal that a low-damage pattern is obtained

with high absorption coefficient. Chmel *et al* [5] investigated the morphology of laser damage of polymer films. Bychkov *et al* [6] studied the laser destruction in polymer material Kesting *et al* [7] studied the pulse and time dependent observations of UV laser induced structures on polymer surfaces. Peterlin and McCrackin [8] showed that the increase in the crystal fraction decreases its free volume of the amorphous phase in some semicrystalline polymers. Nielsen [9] pointed out that polymers are not completely amorphous but are more or less crystalline. Barakat *et al* [10] applied X-ray diffraction technique to investigate the effect of irradiation on fibre. Keller [11] gave a survey of a series of studies on the influence of crystallinity on the radiation induced effects, Suthar *et al* [12] performed X-ray diffraction and IR spectroscopy measurements to study the effect of radiations on the characteristics of polyvinylidene fluoride.

This paper deals with the effect of infrared laser pulses on the X-ray diffraction patterns and IR spectra of cellulose nitrate aiming to investigate the induced physical and chemical changes such as, ordering, disordering and branching. The investigations may enable one to introduce the basis used in constructing a simple sensor of irradiation.

2. Experimental procedure :

Samples :

CR-39 is the trade name of diglycol carbonate. It is a thermo-plastic that combines the optical properties of glass with mechanical and physical properties superior to other plastic. The CR-39 sheets used in this study were manufactured by Pershore, LTD England. It is of density equals 1.32 gm/cm^3 and 300 μm thickness.

LR-115 is cellulose nitrate manufactured by Kodak Pathe, France. It consists of a sensitive cellulose intrate layer of 12 μm thickness on a 100 μm thick polyester support. Its density is 1.42 gm/cm^3.

Makrofol is a polycarbonate foil manufactured by Bayer A G West Germany. It is of 300 μm thickness and density of 1.23 gm/cm^3.

Irradiation facilities :

All samples were exposed to laser pulses for different exposure doses at levels between 0.0 and 7.5 J/cm^2, using an infrared pulsated laser tube of 5 Watt power (Model No. SSL3) USA. The unit is capable of producing 2000 pulse per second with pulse duration 200 nano seconds at 9040 Å. The laser beam were in the form of a circle of 1.8 cm in diameter, and was focused on the sample surface giving pulses once a second.

The X-ray diffraction measurements were carried out with a Philips Powder diffractometer Type PW 1373 goniometer. The diffractometer was equipped with a graphite monochromator crystal. The wavelength of the X-rays was 1.5405 Å and the diffraction patterns were recorded in the 2 theta range (4–80) with scanning speed of 2 degrees per minute.

The infrared measurements were carried out using the Unicam SP1000 infrared spectrophotometer which is a double beam, optical null, precision recording instrument.

This instrument measures in the wave number range 625–3800 cm^{-1}, with wave number accuracy better than ±3 cm^{-1} over 625–2000 cm^{-1} and better than ±9 cm^{-1} over 2000–3800 cm^{-1}.

3. Results and discussions

X-ray diffraction measurements:

Figure 1 shows the X-ray diffraction patterns for the unirradiated CR-39, Makrofol and LR-115 detectors.

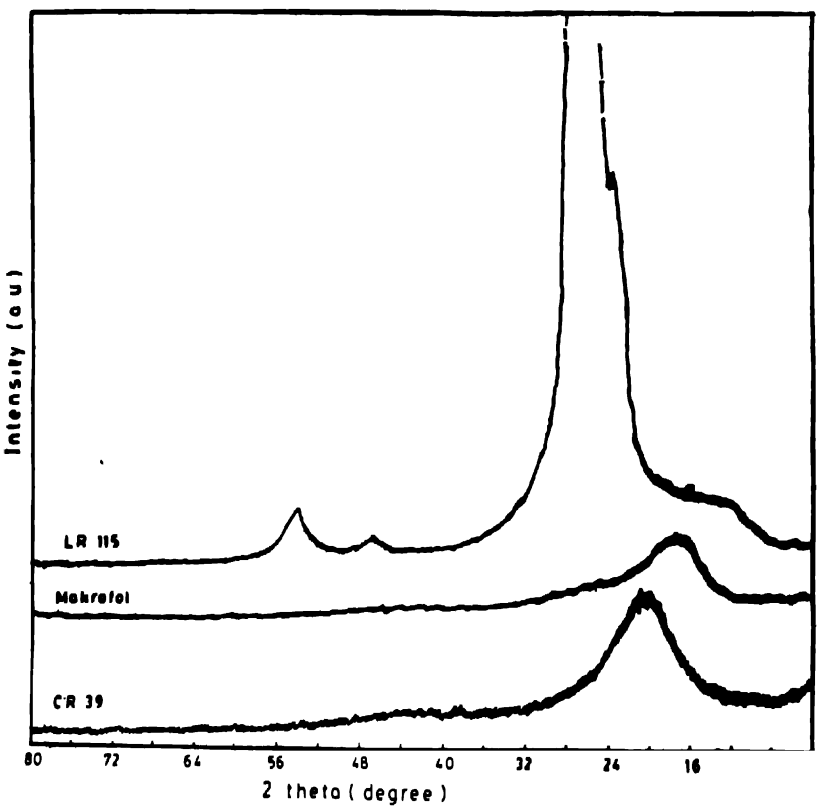

Figure 1. X-ray diffraction patterns for unirradiated CR-39, Makrofol and LR-115 detectors.

From the figure it is clear that the unirradiated CR-39 sample was characterized by the appearance of an amorphous halo extending in the 2 theta range from 12 to 32°. Also, the unexposed Makrofol sample was characterized by the appearance of an amorphous halo extending in the 2 theta range 12–24°. This shows that both CR-39 and Makrofol detectors contain major amorphous phase. While, when the unexposed LR-115 sample was examined by X-ray diffraction the X-ray diffraction pattern (Figure 1)

was characterized by the appearance of an amorphous halo indicating the existence of amorphous regions in addition to discrete reflections at the 2θ values of 26°, 46.8° and 54°, indicating the existance of crystalline regions also. Since the structure of the amorphous phase in the semicrystalline polymer plays a very important role in determining the properties of the material, the LR-115 detector was subjected to further study. The LR-115 samples were exposed to infrared pulsated laser for different exposure doses ranging from 0.0 to 7.5 J/cm^2. X-ray diffraction measurements were carried out on these samples and the corresponding patterns are shown in Figure 2. According to Zachmann *et al* [13] and Miller [14] who suggested methods for distinguishing between the

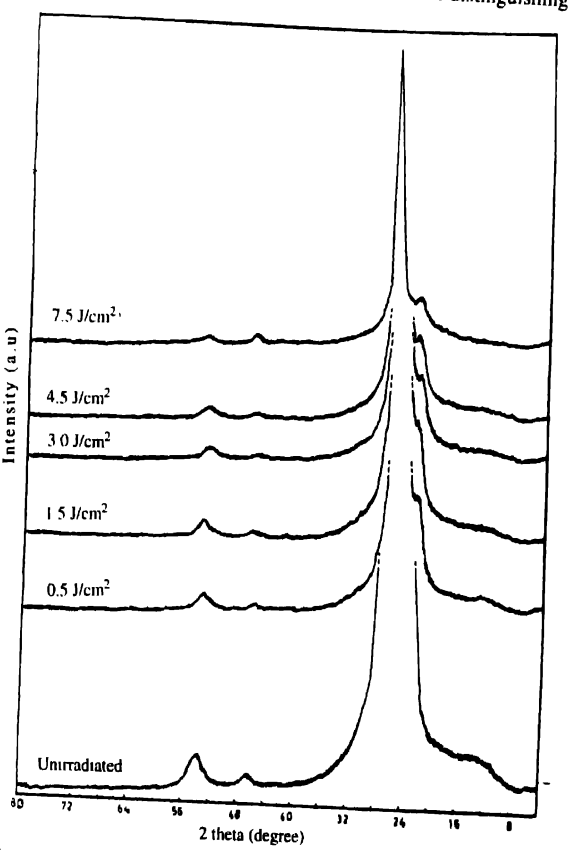

Figure 2. X-ray diffraction patterns for unirradiated and irradiated LR-115 samples.

scattering of X-ray by amorphous and crystalline regions, each of the X-ray diffraction patterns shown in Figure 2 was resolved into several curves (depending on the number of reflections on the X-ray chart) which characterize the scattering by the crystalline and amorphous regions. The area under these curves is proportional to the integral scattering intensity of X-rays. The figure shows that both the integral intensity of the crystalline

reflections (the mass fraction of the crystalline regions) and the integral intensity of the amorphous halo (mass fraction of the amorphous regions) change with changing the laser dose. The integral intensity of amorphous regions (I_{am}) and the integral intensity of crystalline regions (I_{cr}) were calculated and the values obtained are given in Table 1 and

Table 1. The variation of X-ray parameters with laser exposure dose for LR-115 detector

Laser dose (J/cm^2)	Integral intensity of amorphous regions, I_{am} (a. u)	Integral intensity of crystalline regions, I_{cr} (a u.)	Index of crystallinity, ω_c %	Crystallite size, L(Å)
0 0	89.30	46 07	34 0	21.3
0.5	46.65	40 57	44 0	36.7
1 5	43 30	37 60	46.5	40 4
3 0	34.57	32 30	48 3	44.9
4.5	32.24	31.90	49 7	50 5
7.5	20 65	21 36	50 7	57 8

plotted as a function of laser dose in Figure 3(a,b). From the figures it is clear that the integral intensity of the amorphous regions decreases with increasing the laser dose up to 7.5 J/cm^2 indicating the reduction of the amorphous phase in the sample. Also from the figure it is noticed that the integral intensity of the compound crystalline peak decreases with increasing the laser dose until the sharpness of the crystalline peak has been obtained at 7.5 J/cm^2 indicating a high degree of ordering.

The interpretation of the reduction in the integrated intensity of the compound crystalline peak which indicates the decrease in both I_{am} and I_{cr} together with the laser dose can be as follows :

For a semi-crystalline sample as prepared (or as deposited) under certain conditions, nominally, if the sample prepared in its semi-crystalline phase and suffers an annealing within a certain thermal energy range, its degree of ordering or its degree of crystallization will be enhanced as a function of that annealing. If this sample contained traces of an amorphous phase, then with the annealing this phase will disappear causing an increase in the crystalline phase (indicated by enhanced peak intensities). Under certain conditions, the crystalline peak (the dominant peak) may decrease due to (i) presence of an intermediate phase which can volatile with the annealing. (ii) If a large surface change of the sample arises due to an injection of high dose of destructive radiation which certainly affects the degree of roughness of the surface beside the vaporization of surface atoms.

Values of the apparent degree of crystallinity or the index of crytallinity ω_c were calculated for the LR-115 polymer since the crystalline and amorphous scattering in the diffraction pattern could be differentiated from each other. The degree of crystallinity was considered to be the ratio of the integrated crystalline scattering to the total scattering, both crystalline and amorphous. The obtained values are also given in Table 1 and plotted as a function of laser dose in Figure 3(c). The index of crystallinity ω_c showed an increase on

increasing the laser dose indicating the increase of the mass fraction of the crystalline phase in the sample.

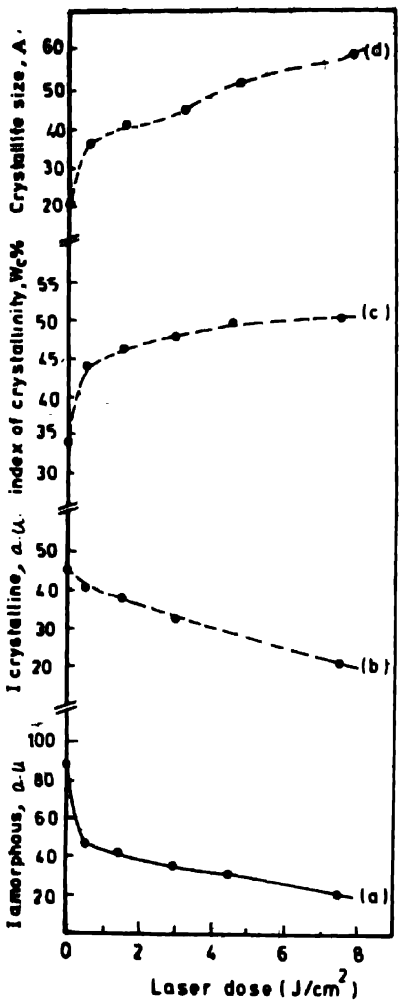

Figure 3. The dependence of (a) the integral intensity of the amorphous regions (I_{am}), (b) the integral intensity of the crystalline regions (I_{cr}), (c) index of crystallinity (ω_c) and (d) crystallite size (L) on the laser dose.

Approximate indicative size of the crystallites (L) were calculated by means of the Scherrer equation [15,16].

$$L = \frac{0.89\lambda}{\Delta W \cos\theta},$$

where ΔW is the peak's width at the half of maximal intensity and λ is the wavelength of X-rays. The values obtained are also given in Table 1. Figure 3(d) shows the dose dependence of the crystallite size. From the figure, it is clear that the crystallite size increases with increasing the laser dose indicating also a high degree of ordering. It is also

noticed that the intensity of the crystalline peaks at $2\theta = 26$, 46.8 and 54 and also the intensity of the amorphous peak at $2\theta = 23.2$ varies with the variation of the laser dose (Table 2). This means that the mass fraction of the crystalline and amorphous phases changes with changing laser dose. The interpretation of the above results can be explained as follows :

Table 2. The variation of peak intensity with laser dose for LR-115 detector.

Non exposed		0.5 J/cm^2		1.5 J/cm^2		3.0 J/cm^2		4.5 J/cm^2		7.5 J/cm^2	
$2\theta°$	I	$2\theta°$	I	$2\theta°$	I	$2\theta°$	I	$2\theta°$	I	$2\theta°$	I
23.2	17.9	23.2	8.3	23.2	8.3	23.2	5.9	23.2	4.5	23.2	3.5
26.0	41.5	26.0	36.1	26.0	35.4	26.0	33.2	26.0	35.8	26.0	20.4
46.8	0.9	46.8	0.4	46.8	0.25	46.8	0.0	46.8	0.0	46.8	0.6
54.0	2.0	54.0	1.0	54.0	1.0	54.0	0.7	54.0	0.6	54.0	0.5

By exposing the sample to laser light, the sample surface rises to the vaporization temperature and begins to vaporize. The evaporated material will flow away from the centre of irradiation due to the thermal gradient leaving behind it a resultant pit. After stopping the stimuli, the molten material will begin to recrystallize at the colder regions in the surroundings of the pit. This leads to the growth or multi-layered crystals and different shaped grains and grain boundaries. Similar effect was observed before [17].

Infrared spectra of LR-115 detector :

Figure 4 shows the infrared spectra of unirradiated and irradiated LR-115 samples. From the figure it is clear that the half band width $\nu_{1/2}$ of the infrared absorption bands were slightly affected by the laser dose. On this basis and since the intensity of the absorption band is equal to $(\pi/2)\ \nu_{1/2} \log (I_0/I)$, the absorbance $\log (I_0/I)$ could be taken as a direct measure of the intensity. Values for the absorbance (A) and $\log (I_0/I)$ at the maximum of the absorption band over the range (0–3800 cm^{-1}) were obtained and are given in Table 3.

Figure 5 shows the dependence of the absorbance (A) (measured at different wavenumbers) on the laser dose. It is clear from the figure that the absorbance showed a linear increase up to a maximum value around 4.5 J/cm^2 due to the existence of amorphous regions followed by a decrease on increasing the laser dose up to 7.5 J/cm^2 due to the high degree of ordering. The interpretation of the above figure can be explained according to Tobin [18] that a majority of the absorption bands in the infrared spectra of polymers are associated with both crystalline and amorphous regions. A few absorption bands, however, are produced by the amorphous regions only, due to the loss of symmetry by the cooling of the chain in amorphous regions. Also, according to Zbinden and Rudolf [19] who assigned specific absorption bands as crystalline and amorphous, we may define the "crystalline band" as one which does not appear in the spectra of the completely amorphous polymer and becomes more intense with the increase of the crystalline character

conversely, an "amorphous band" is one which does not appear in the spectra of the crystalline polymer and become more intense with the increase of the amorphous character. Under these previous definitions and according to Mostafa [20], it can be pointed out that all the bands that increase in intensity with the increase in the amorphous character may be called amorphous bands. On the other hand, all bands that decrease in intensity with the decrease in crystalline character may be called crystalline bands. These show that all the amorphous bands in the LR-115 detector tend to be crystalline bands on increasing the laser dose up to 7.5 J/cm^2 (and this agrees with the X-ray diffraction results) due to the explanation that : by focusing the light of high power pulsed laser on a target surface, the material surface rises to the vaporization temperature and begins to vaporize. The material evaporated is partially burnt, and this gives rise to gas bubbles of high pressure and temperature. The gas pressure produces near the bubbles large stresses and initiates the development of cracks which proceeds into the target. The cracks become wedged a part by heated gas. During the course of crack expansion, the hot gas carburizes the crack walls, enhancing further light absorption.

4. Conclusions

The X-ray diffraction measurements indicated that the exposure of the LR-115 samples to laser pulses, leads to the growth of multi-layered crystals and different shaped grains and grain boundaries, *i.e.* the samples tend to be crystalline. This conclusion was drawn since both the index of crystallinity and crystallite size increased on increasing the laser dose while the mass fraction of the amorphous phase decreased. The infrared measurements indicated that the infrared pulsated laser enhances the light absorption of the LR-115 polymer up to a certain dose (4.5 J/cm^2) then it enhances the light transmission of the polymer due to the high degree of ordering obtained at higher laser doses (4.5–7.5 J/cm^2).

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